Near-Field Polarimetry of Self-Assembled Polymer Systems

Michael J. Fasolka

Polymers Division

National Institute of Standards and Technology, Gaithersburg, MD

NIST
Optical Technology Division
Lori S. Goldner
Jeeseong Hwang
Polymers Division
Kathryn Beers

Massachusetts Institute of Technology
Dept. of Materials Science and Engineering
Augustine Urbas
Peter DeRege
Edwin L. Thomas

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Outline

1) Discuss *Near-Field Scanning Optical Microscopy* (NSOM) and NSOM Polarimetry.

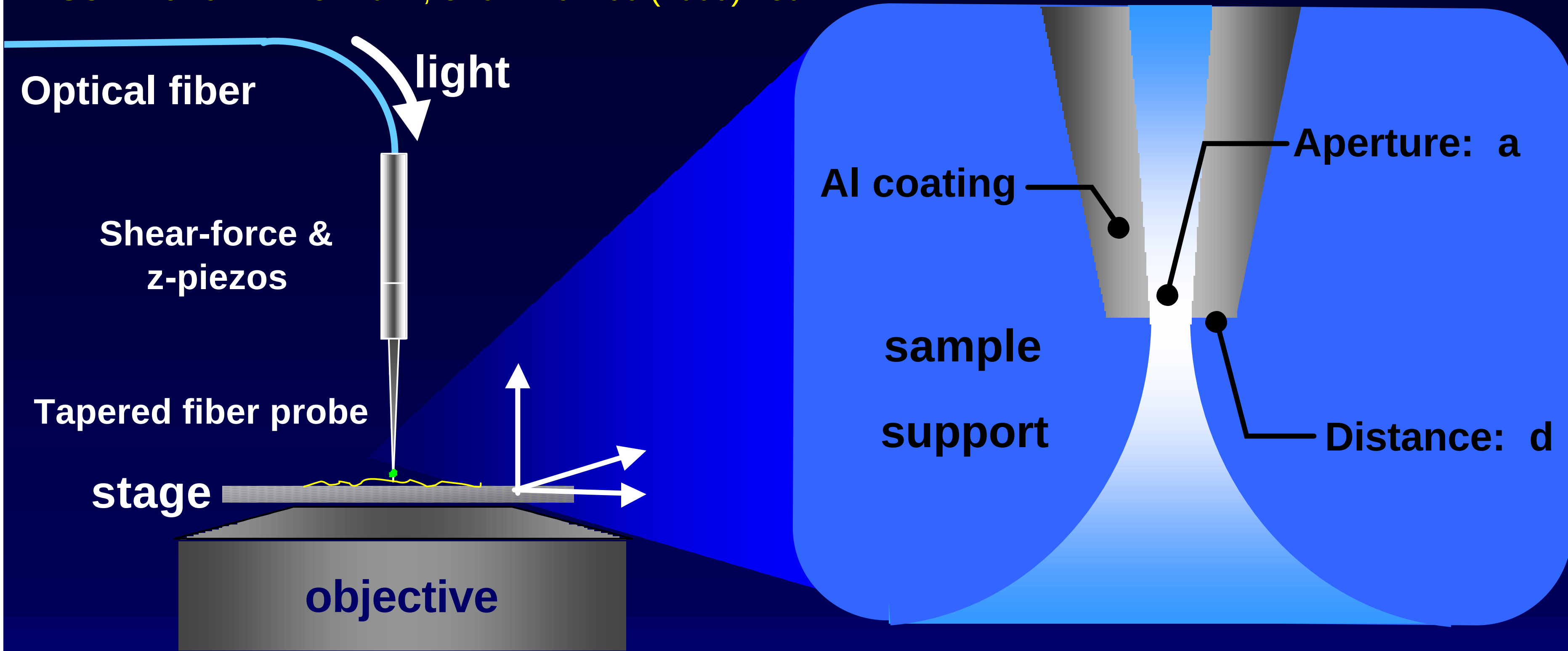
- An scheme for quantitative NSOM polarimetry based upon improved polarization modulation (PM) techniques.

2) Demonstrate utility of PM-NSOM through studies of two self- assembling polymer systems:

A) Microphase separated Photonic Block Copolymers
B) Thin film isotactic polystyrene crystallites

Aperture NSOM

NSOM Review: R. C. Dunn, *Chem Rev.* **99** (1999) 2891.



- Aperture, **a**<<l (40-150 nm) *Maximum resolution:* ***a***
- Distance, **d**<<l (5-10nm)
- **d** maintained as sample scanned under probe via force feedback.
  - – Topography information also collected as in AFM.
- Image generated from transmitted intensity at each point (x,y).

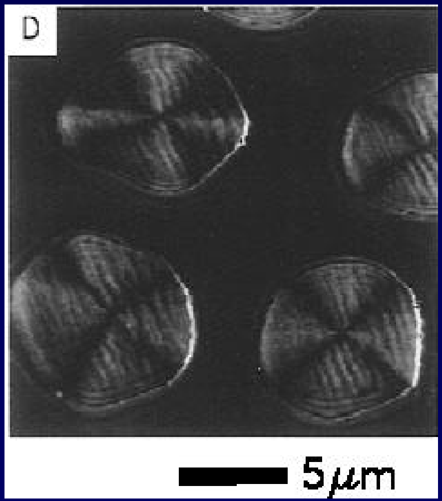
Motivation

~100 nm resolution of NSOM

Morphology and molecular orientation illuminated by polarized light

NSOM Polarimetry for nano-scale characterization

Qualitative NSOM Polarimetry



e.g.: Observations of birefringence in kevlar fibers via NSOM.

"Crossed polarizer" experiment

H. Ade, R. ToledoCrow, M. VaezIravani, and **R. J. Spontak**, Langmuir 12, 231 (1996)

Quantitative NSOM Polarimetry

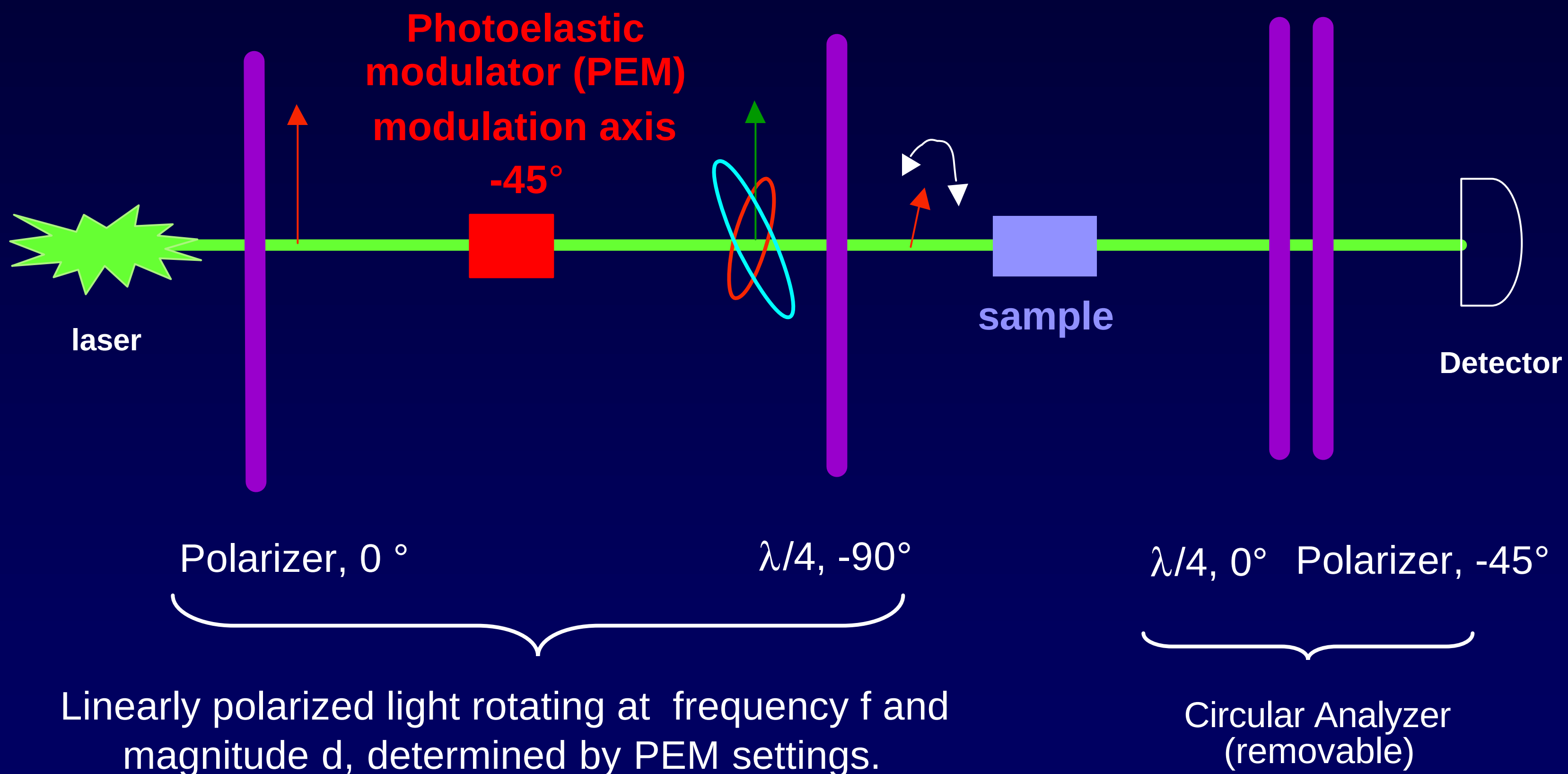
(The aim of these studies)

Measurement and *mapping* of polarimetric optical properties with NSOM resolution.

- Dichroic ratio: $D=(x-y)/(x+y)$
- Angle of Dichroic Axis: ϕ_D
- Phase retardance: θ (birefringence)
- Angle of fast axis: ϕ_B (birefringence)

Polarization Modulation Polarimetry

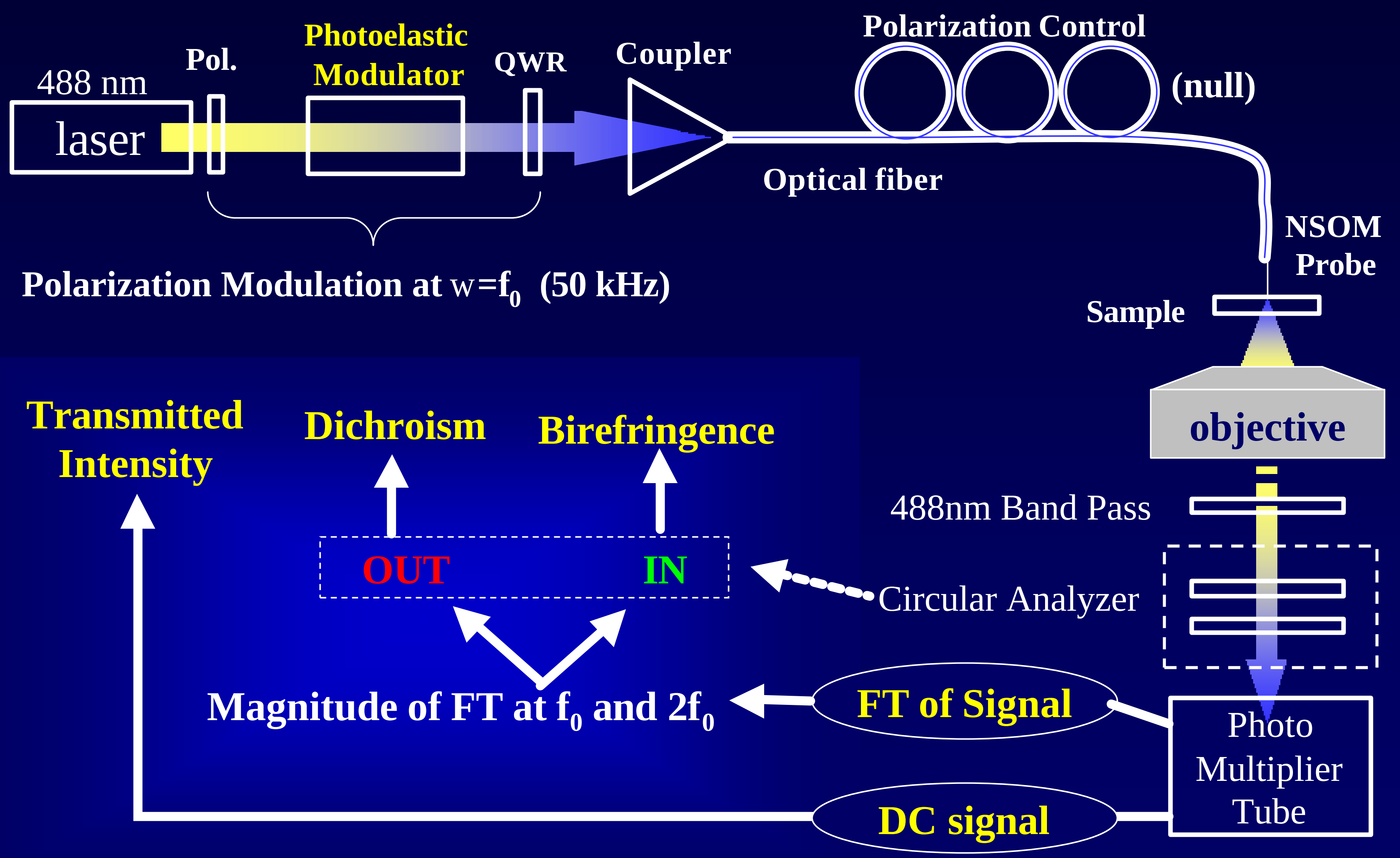
e.g.: S. J. Johnson et al., Colloid Interface Sci. **104, 440 (1985)**



Analysis of transmitted AC intensity signal yields polarimetric quantities associated with sample dichroism and birefringence.

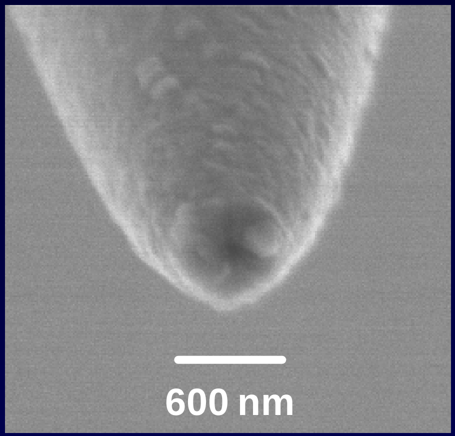
PM-NSOM Polarimeter

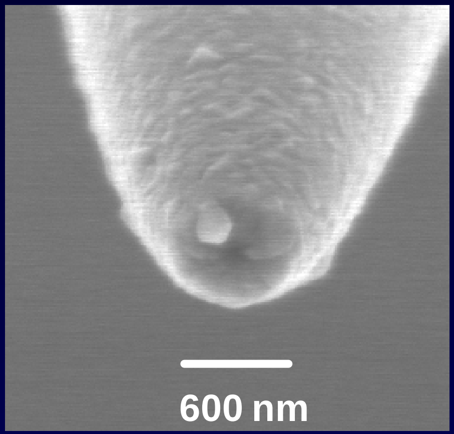
(After McDaniel et al, *Applied Optics* **37**(1) p.84 1998)

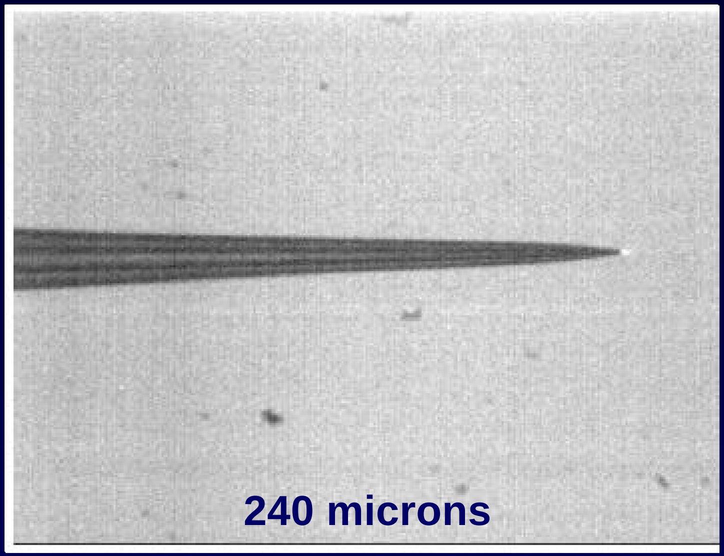


NSOM aperture probes

NIST







- Fabricated at NIST (Pat Connelly)
- Pulled single mode optical fiber
    - 130 nm Al coating
- Aperture used in this study have width 100-120 nm (by SEM).

These aperture probe tips are themselves dichroic!

Optical properties of the probe obscure those of the sample!

<u>Barriers to Quantitative PM-NSOM</u>

Experimental Technique/Analysis must account for these effects:

1. **Tip dichroism on fiber birefringence null**

   While stress-induced birefringence in a bare fiber can be “nulled” via fiber paddles, we find that tip dichroism results in a *residual birefringence* that is not removed.

2. **Tip dichroism on sample dichroism**
3. **Tip dichroism on sample birefringence**
4. **Sample dichroism on sample birefringence**

Incorporating all of these effects (exactly) using Jones/Mueller Matrices results in large, intractable analysis equations.

Our approach:

1. **“Thin film” approximation: tip and sample quantities are small ($D<0.1$, $q < 0.1$ rad) → uncertainty ~1%**
2. ***Explicit* measurement of tip properties first! These are used to calculate sample properties.**

Improved PM Analysis Formalism

Lori Goldner (Physics, NIST)

NIST

Fourier Analysis of Detected Intensity f(t):

$$f(t) = A_0 + A_1 Sin(wt) + A_2 Cos(2wt) + ...$$

Measurement of Dichroism and ϕ_D (analyzer out):

tip | sample

$$R_{1w} \equiv \frac{A_1}{A_0} \cong 2J_1(d)\left[D_t Sin(2j_d^t) + D_s Sin(2j_d^s)\right]$$

$$R_{2w} \equiv \frac{A_2}{A_0} \cong 2J_2(d)\left[D_t Cos(2j_d^t) + D_s Cos(2j_d^s)\right]$$

J_n are n[th] order Bessel functions.

Measurement of retardance q and fast axis angle f_b (analyzer in):

$$B_{1w} \equiv \frac{A_1}{A_0} \cong R_{1w} + 2J_1(d)\left[Sin(q_t)Cos(2j_b^t) + Sin(q_s)Cos(2j_b^s)\right]$$

$$B_{2w} \equiv \frac{A_2}{A_0} \cong R_{2w} - 2J_2(d)\left[Sin(q_t)Sin(2j_b^t) + Sin(q_s)Sin(2j_b^s)\right]$$

we measure: ***A_0 = DC intensity***

A_1 = Intensity at 1w

A_2 = Intensity at 2w

Measurement Procedure

NIST

We start with the sample out

1. **Fiber birefringence is "nulled" through fiber paddles.**
   - **A_1 and A_2 monitored and minimized**

Sample contributions are 0!

2. **Tip dichroism is measured via R_{1w} and R_{2w}**
   - If tip dichroism>0.1, replace tip, go to **1**
3. **Residual tip birefringence is measured via B_{1w} and B_{2w}**
   - Tip dichroism value is used in calculation

Sample is inserted

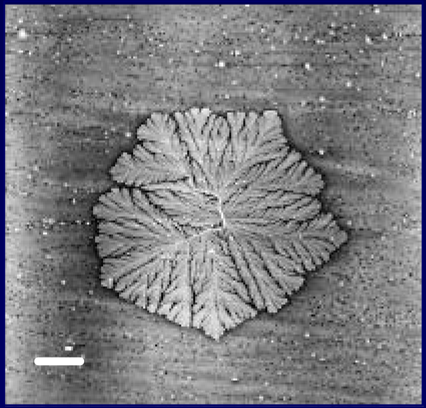
4. **Sample Dichroism is measured (128 X 128 pixel image)**
   - Tip dichroism value is used in calculation
5. **Sample Birefringence is measured (image) (Analyzer in)**
   - Tip dichroism, birefringence, and sample dichroism are used in calculation.
6. **Tip properties are re-measured to check for gross changes during scan. (Potentially, the data must be discarded.)**

Application Examples:

1. **Photonic Block Copolymer Specimens**
   A. Urbas, P. DeRege & E.L. Thomas
   Dept. Materials Science and Engineering, MIT

   Objectives:
   - **Image individual microphase domains and defects with visible light NSOM polarimetry.**
   - **Examine contrast mechanisms**

2. **Thin Film Polymer Crystallites**
   K. Beers
   Polymers Division, NIST



   Objectives:
   - **Probe crystallites with PM-NSOM**
   - **Consider ramifications on structure and formation**

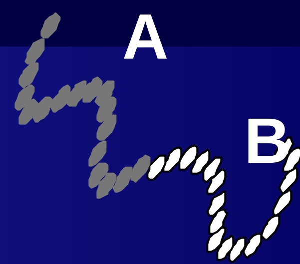
Photonic Block Copolymers

A. Urbas, P. DeRege, E.L. Thomas

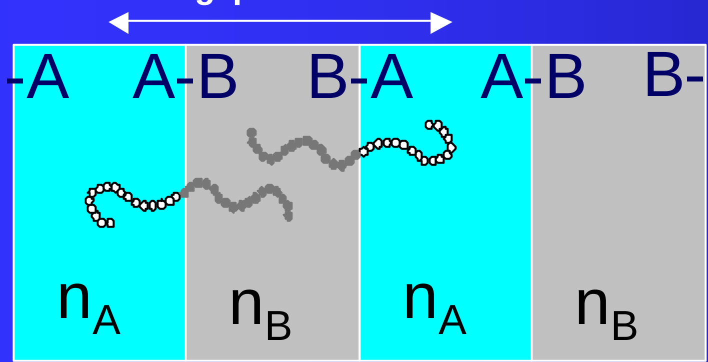
Urbas et al., *Macromolecules* **32** (1999) 4748.
Fink et al., *J. Lightwave Tech.* **17** (1999) 1963.

Recent synthetic efforts have produced a variety of block copolymers (BCs) with ultra-high molecular weight.

These materials self-assemble on length scales sufficient for photonic activity.



$L_0 \approx \lambda_{gap}/4n > 100\,\mathrm{nm}$



- **Tunable band structure:**
  - **L_0 (molecular weight)**
  - **Motif (Composition)**
- **Amenable to solvent and film processing**
- **Mechanically Flexible**
- **Solid foundation of prior research**

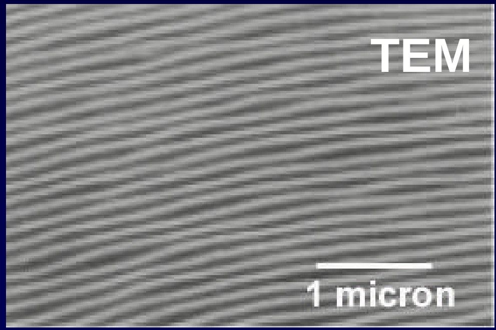
Development of photonic BC requires characterization of *local* optical structure at the scale of single defects and domains, as these may dictate device function. (PM-NSOM!)

Materials Preparation

NIST

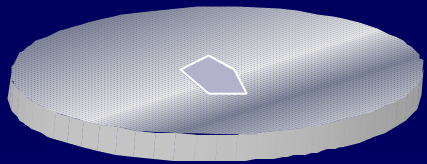
Materials Synthesis and Preparation: (MIT Team)

- Symmetric Polystyrene-b-Polyisoprene block copolymer
  - Sequential Anionic Synthesis, Low O_2 Drybox
  - MW= 470k/580k, PDI=1.02
  - Lamellar Motif, **L_0»240nm**



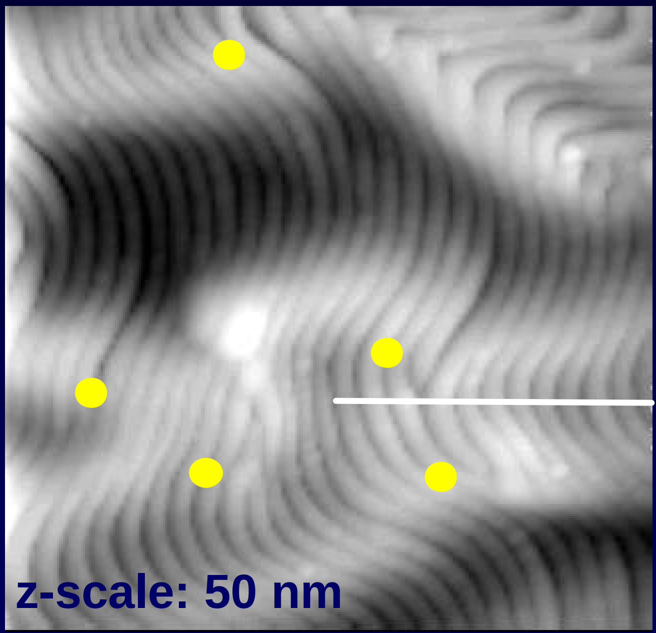
- Cryogenic ultramicrotomy of sheer aligned specimens
  - 100nm thick sections deposited onto glass coverslips

- 2 hour staining with OsO_4 vapor (crosslinks PI)
  - Increase optical contrast
  - stiffen PI – better shear feedback

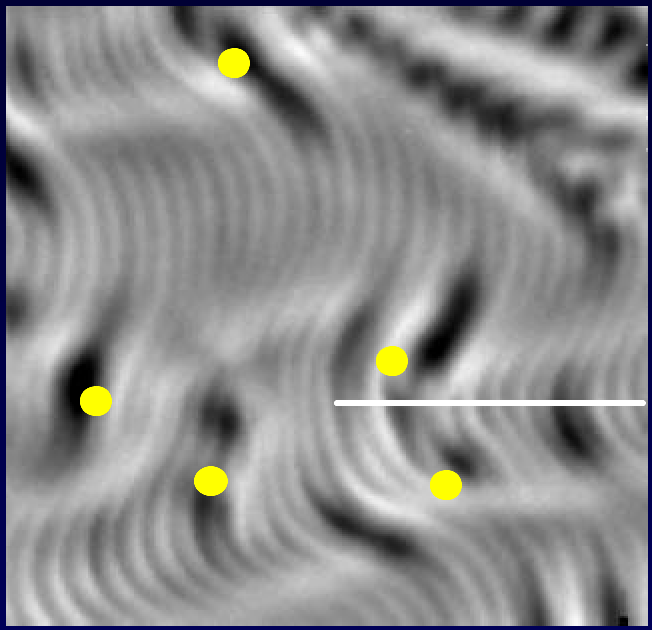


Transmission NSOM

Topography



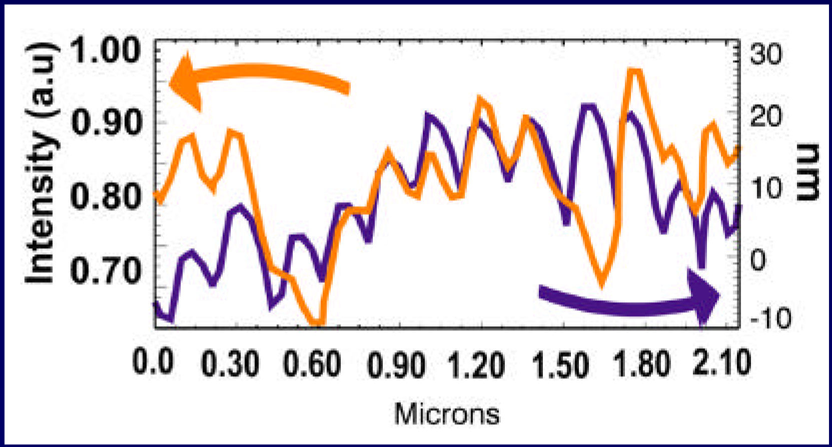
Tramsmission



- Single domains resolved
- Defect structures show exaggerated contrast

SCATTERING CENTERS?

2.1 mm section (white line)



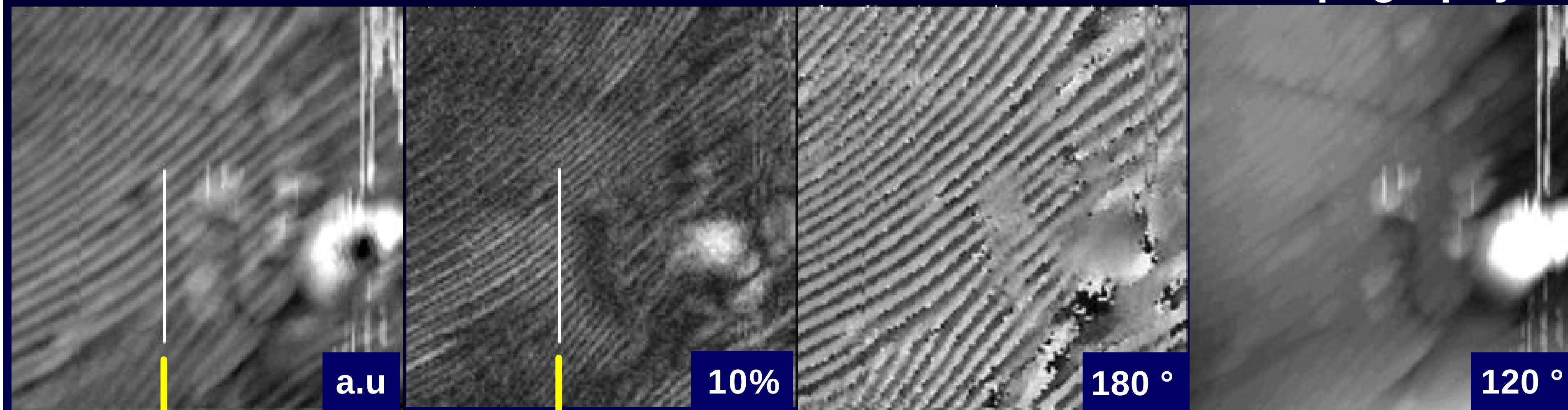
Darker domains are correlated with lower domains:

Dark phase is stained PI

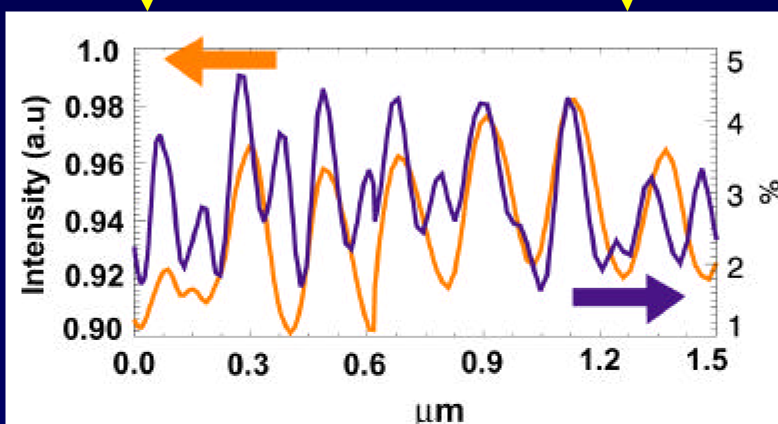
Dichroism Images

(relative)

Transmission | Dichroism | Dichroic Axis Ð | Topography



All images are 4mm X 4mm



- Axis angle alternates between domains.

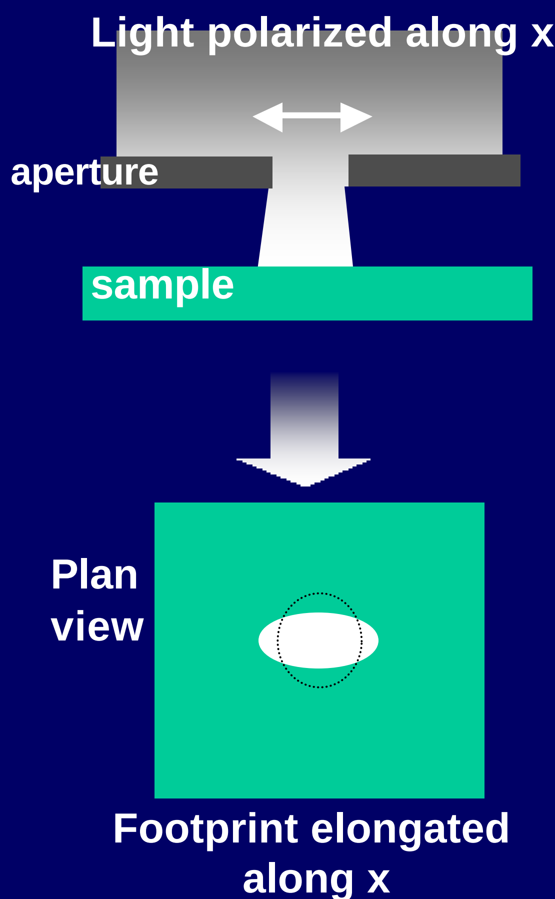
Mechanism for this pattern of dichroism?

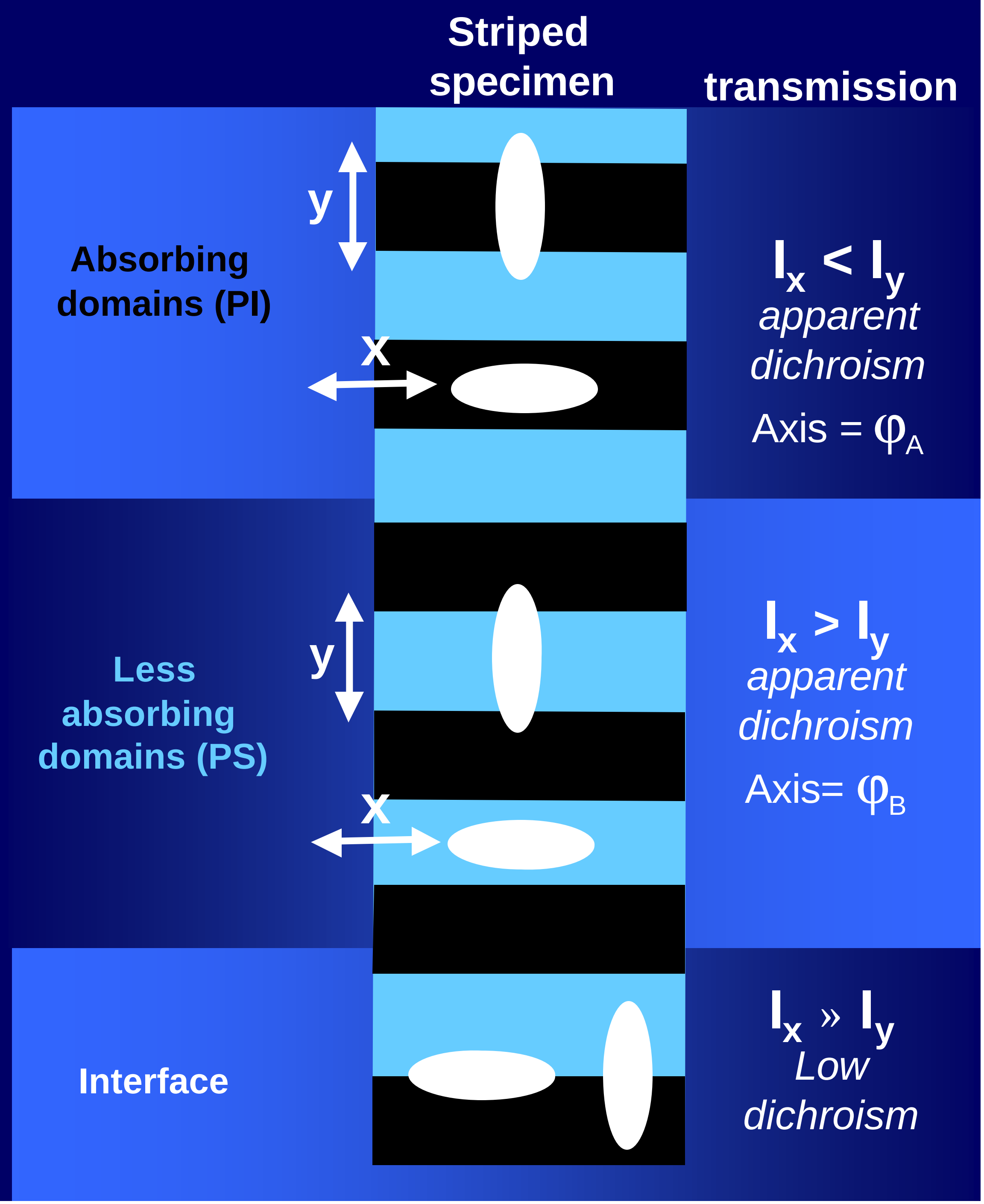
- PS domains are more dichroic
- Dichroism minimum at PS/PI interface

Hypothesis

Bethe-Bowkamp model

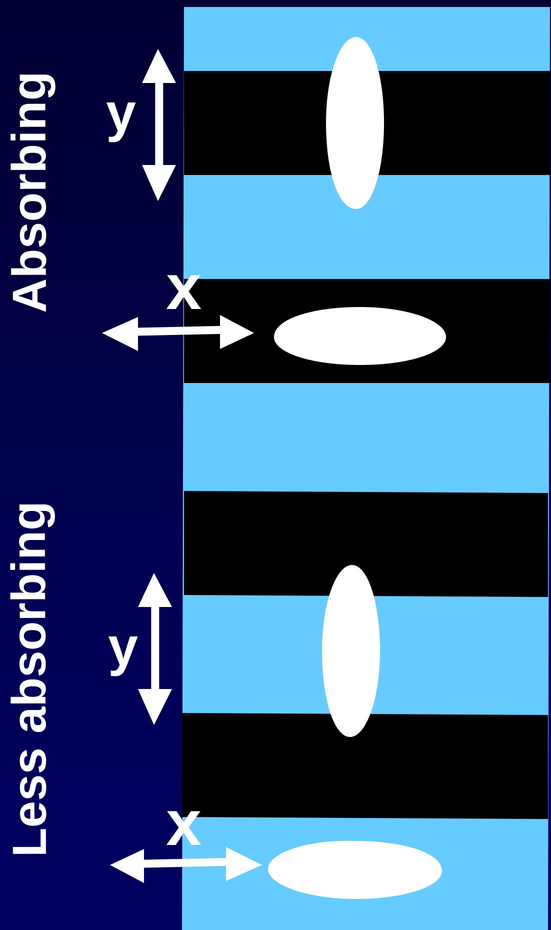
Anisotropic Light Footprint

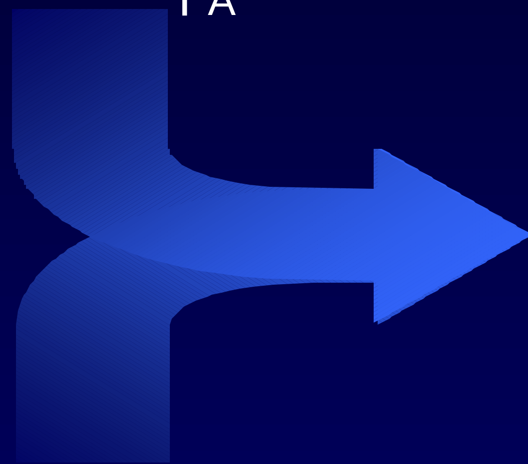




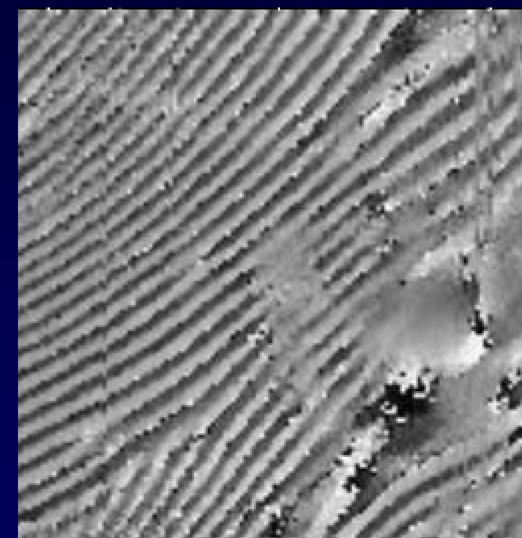
H. A. Bethe, Phys. Rev. 66, 163 (1944); C. J. Bowkamp, Philips Res. Rep. 5, 401 (1950)

Bethe-Bowkamp Hypothesis:





Observed dichroic axis changes by ≈ 90° between domains.



4mm X 4mm

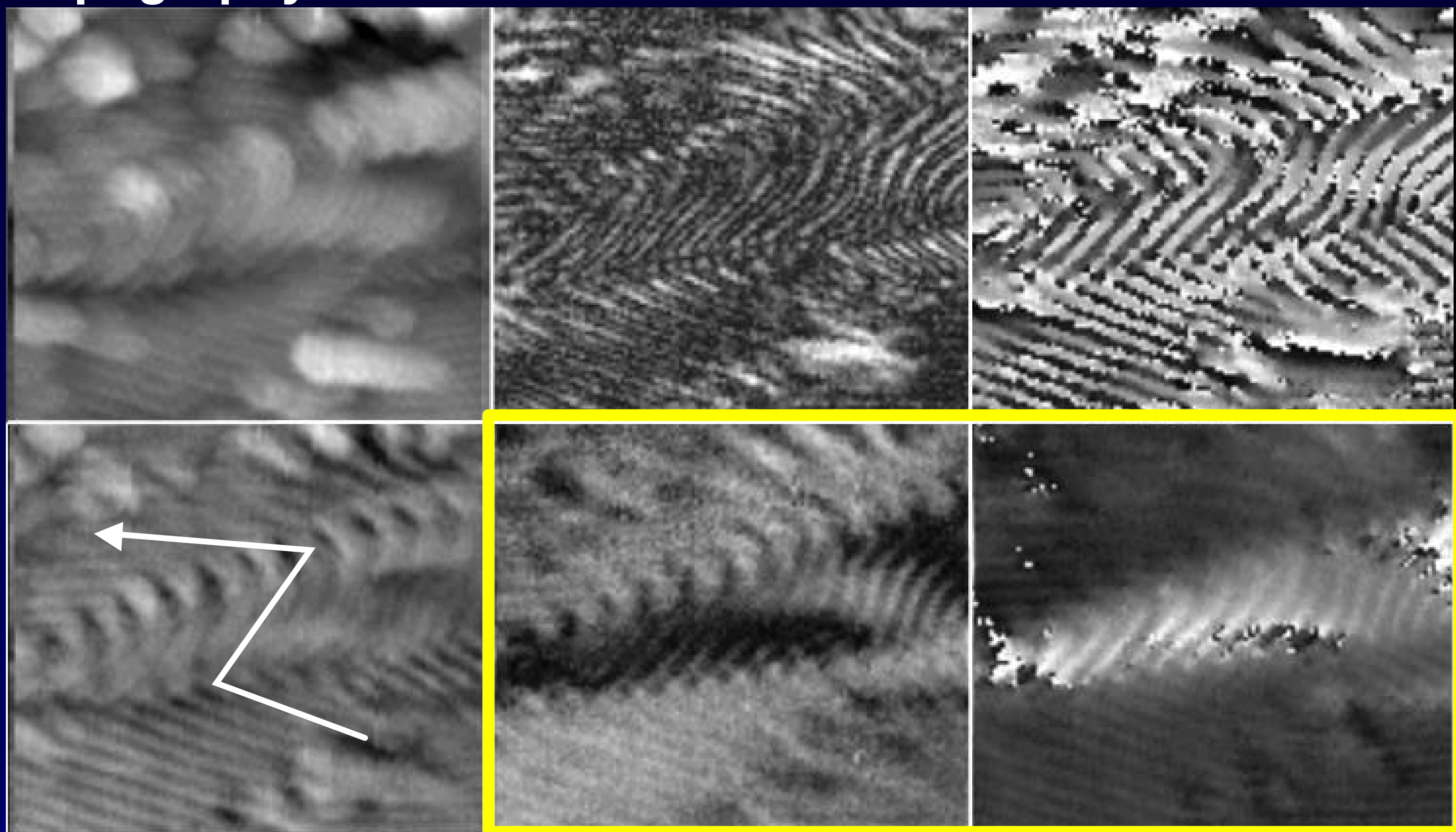
However, if this hypothesis is true, the measured dichroism is in part an NSOM artifact!

Modeling (G. Bryant NIST) is in progress.

Birefringence Images

(relative)

Topography: 43 nm **Dichroism: 4%** **Dichroic Axis Ð: 180°**



Transmission: a.u. **Retardance: 7°** **Fast Axis Ð: 180°**

(relative)

Symmetric twin boundary defect in PS-b-PI photonic BC

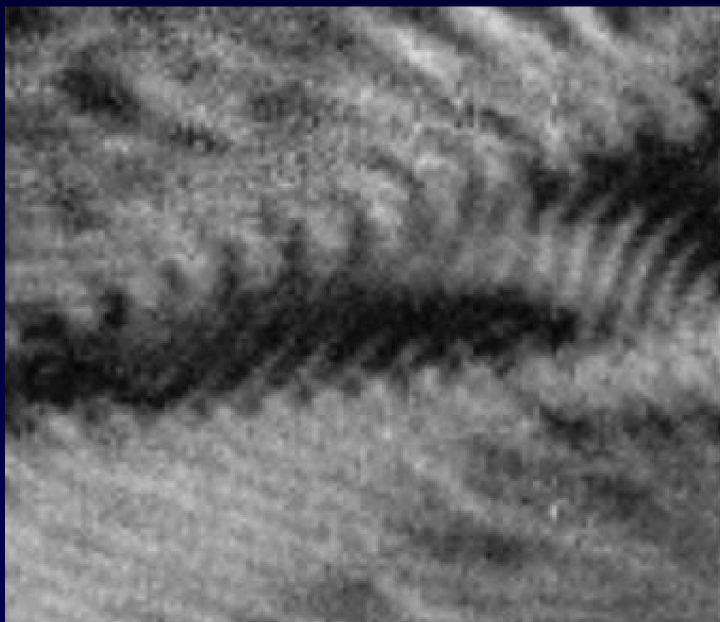
Images are 4 mm wide

- **Dichroism images and tip properties used in birefringence measurements.**

Birefringence Contrast Mechanisms

Retardance q: 7° range

q = Dn *f(s)* l t

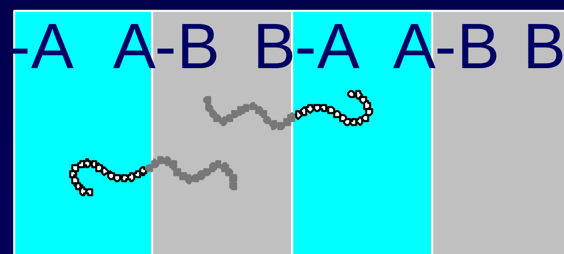


t: thickness   l : 488nm

Dn: " Intrinsic birefringence" = n^{II} - n$^{\perp}$

Fully extended polymer chain

f(s): degree of chain elongation, "stress"



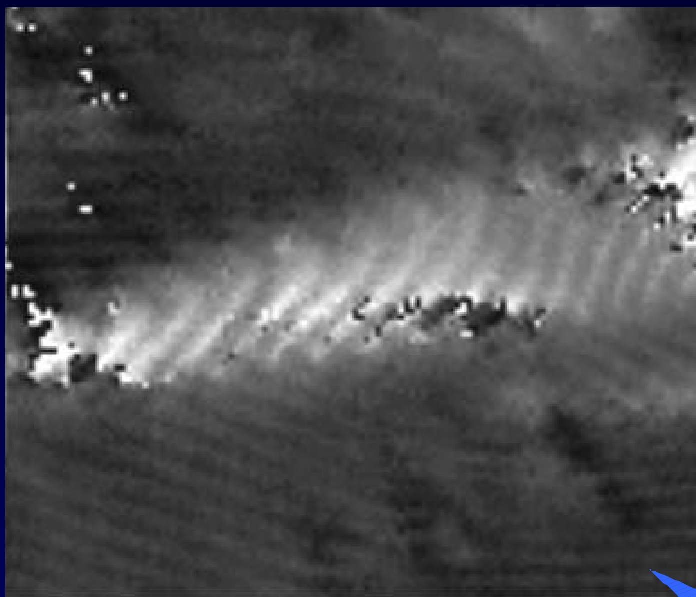
In BCs, chains are slightly extended $\perp$ to the domain interface

Interdomain contrast (slight) is due to differences in Dn between PS (0.192) and PI (»0.1).

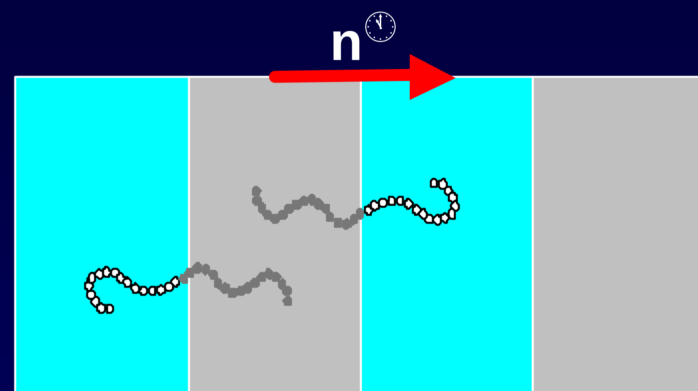
The stronger contrast across the defect is due to t, and *f(s)* which is related to the local stress. Projection effects are also likely.

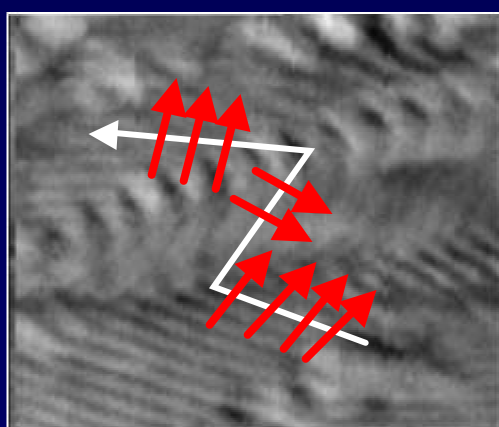
Birefringence Contrast Mechanisms

Fast Axis $\propto \phi_B$: 180° range



Due to chain elongation, the fast (low-n) axis runs ⊥ to the domain interface.





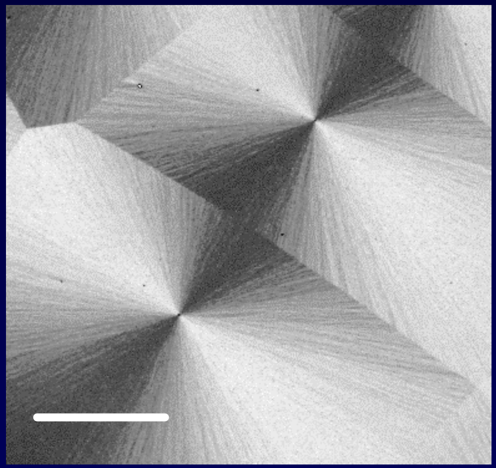
Transmission: a.u.

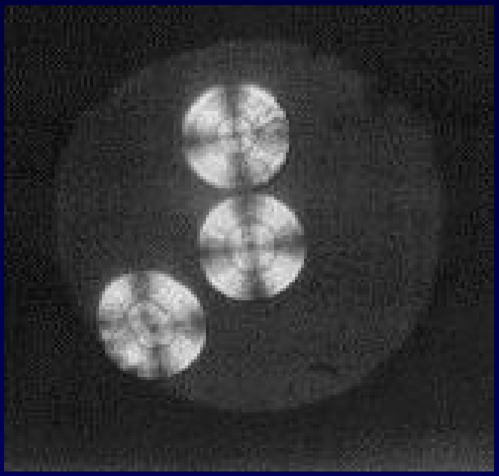
As the lamella bend into and out of the twin, the fast axis angle increases (brighter) and then decreases.

Images are 4μm wide

Polymer Crystals

Classical polarimetry was essential to determining the structure of spherulitic polymer crystals in the bulk.





Crossed polarizer optical microscopy of polymer spherulites.

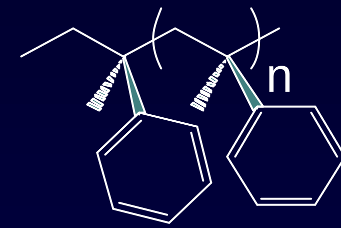
Layers of folded chains (lamella) arranged in a radial fashion. Birefringence results in “cross pattern.”

However, ultra-thin/small crystals are not amenable to study by far-field techniques.

Low signal and/or below the diffraction limit

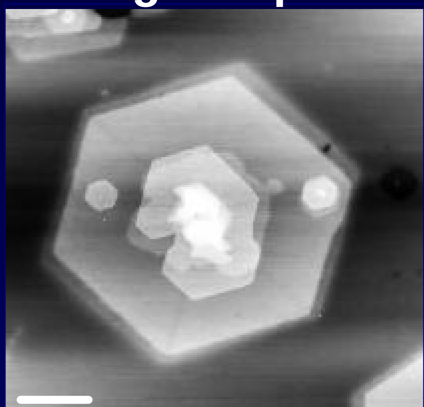
Thin Film Polymer Crystallites

K. Beers (Polymers Division, NIST)

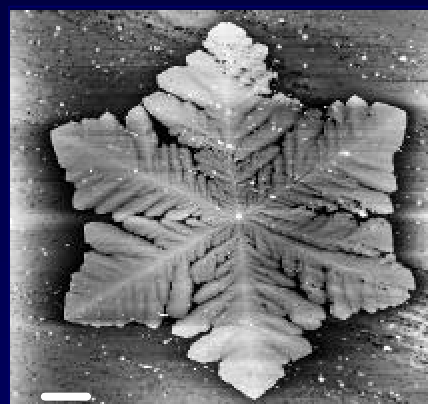


Isotactic Polystyrene (iPS) exhibits a range of crystalline forms depending upon the film thickness and crystallization temperature

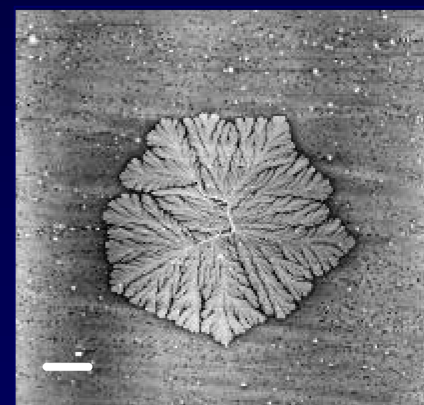
Hexagonal plates



snowflakes

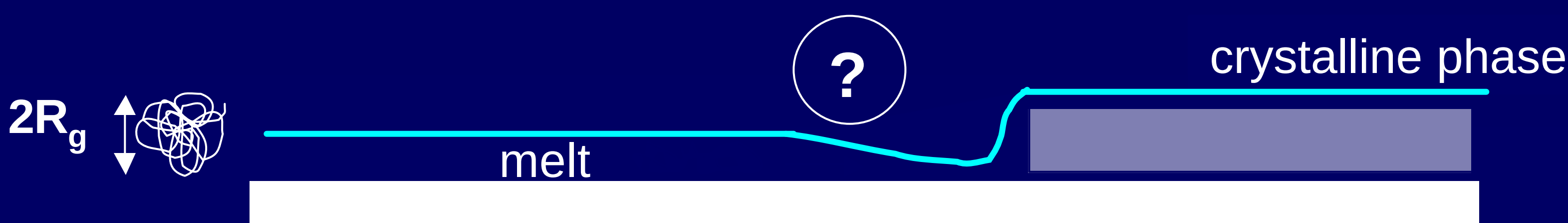


Random dendrites



AFM images
Scale bar is 10mm

How are chains folded in non-spherulitic crystals?
How is crystallization achieved in these confined systems?
Thickness is on the order of random coil dimensions...



PM-NSOM Experiments

NIST

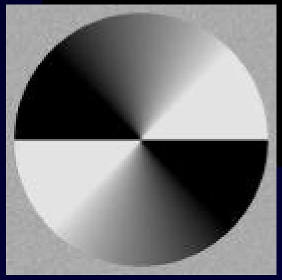
We recently examined two systems:

1) Disk-like Crystallites (2D spherulites)
   Thickness: 60nm

2) Random Dendrites
   Thickness: 15nm

- 100K MW iPS
- Spun cast from Toluene onto glass coverslips treated with hydrophobic SAM (prevents dewetting).
- Crystallization T: 160 °C
- Growth arrested by quenching after 1 hour

PM-NSOM of iPS crystallites

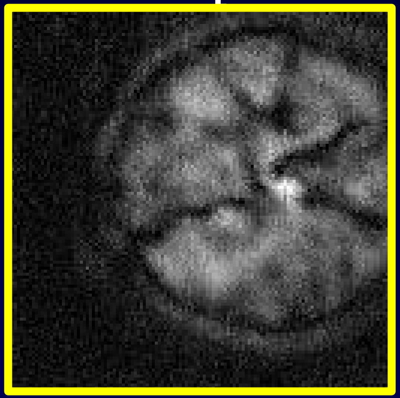


Disk-like crystallite (2D spherulite), 60nm thick

Topography [40nm]

Transmission

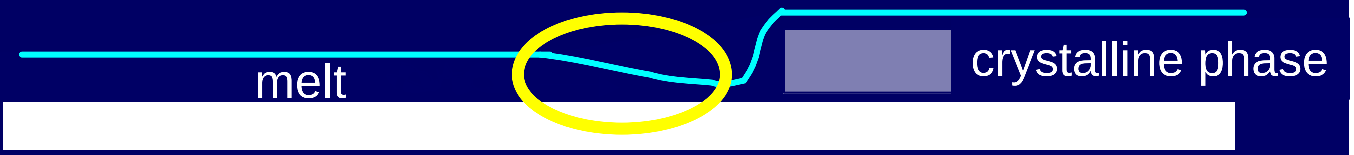
Retardance [110 mrad]



Fast axis [0-p]

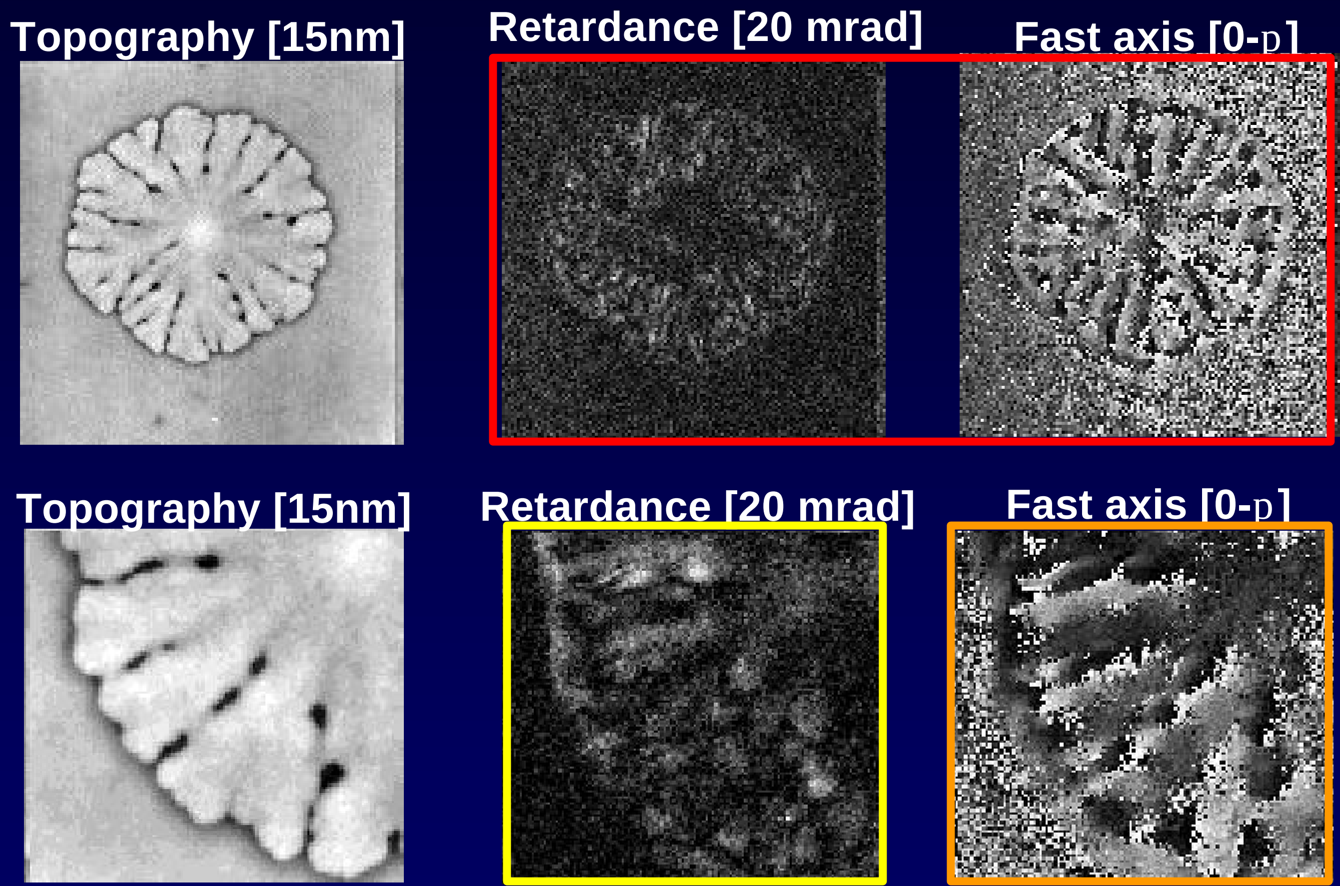
- **Transmission illuminates voids due to solvent evaporation.**
- **Fast axis image shows radial distribution of crystalline lamellae.**
  Many defects in the crystal structure are apparent.
- **Retardance map shows areas with ordered chains.**
  There is a "ring"of ordered material outside the crystallite!
  This suggests that the chains elongate before crystallizing.
  "Pre-crystalline" chains at the periphery are radially arranged.

Images are 6mm wide



Dendritic iPS crystallites

Francoise Renaldo (SupOptique, France)



4.8 µm wide

8ms/point

2.4 µm wide

16ms/point

- **Very low signal (only 15nm thick!). Longer collection time required.**
- **Fast Axis image shows dendrite arms have complex structure with many chain orientations.**
- **Retardance map suggests "pre-ordering" on spherulite periphery.**

Summary

- NSOM polarimetry demonstrated as a tool for characterizing local optical structure of thin polymer specimens
  - Improved PM-NSOM measurements account for:
    - aperture dichroism
    - aperture birefringence
    - sample dichroism.
  - Quantitative measurements of sample dichroism and birefringence

- PM-NSOM techniques were used to image self-assembled polymer systems.
  1) Photonic Block Copolymer Films
     Single microphase domains and defects resolved
     Contrast mechanisms discussed
  2) Thin iPS crystallites
     PM-NSOM illuminates crystallite structure and provides clues to crystallite formation.

Acknowledgements and Thanks:

NIST

- Lori Goldner, Jeeseong Hwang (PL, NIST)
- Augustine Urbas, Peter DeRege, E.L. Thomas (MIT)
- For helpful conversations:
  - Garnett W. Bryant (PL, NIST)
  - Hoang-Phi Nguyen, Sophie Nougier, Francoise Renaldo (SupOptique, France)
  - Thomas Germer (PL, NIST)
- For NSOM probe fabrication:
  - Patrick Connelly
- For funding:
  - National Research Council Post-doctoral Associateship
  - NIST PL

Advertisements

NIST

Interested in NSOM? NSOM Polarimetry?

Post Doctoral positions are available in the Physics Lab of the National Institute of Standards and Technology!

Contact Lori Goldner at: lori.goldner@nist.gov
(Or approach me here…)

Interested in Combinatorial and High-Throughput methods for Materials Research?

The NIST Combinatorial Methods Center specializes in combi techniques for Materials Science.

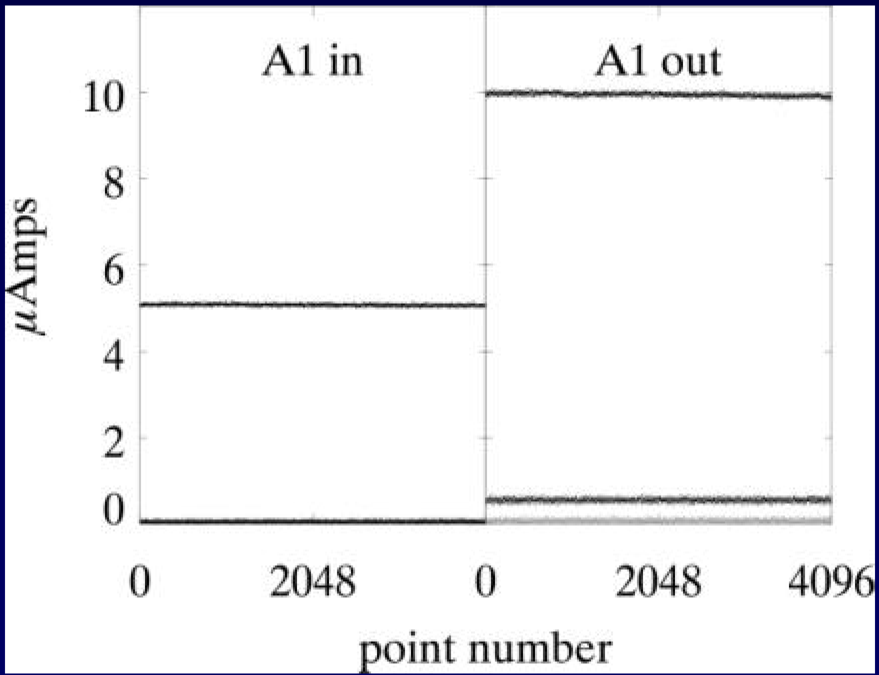
Ask me for literature,
or visit www.nist.gov/combi

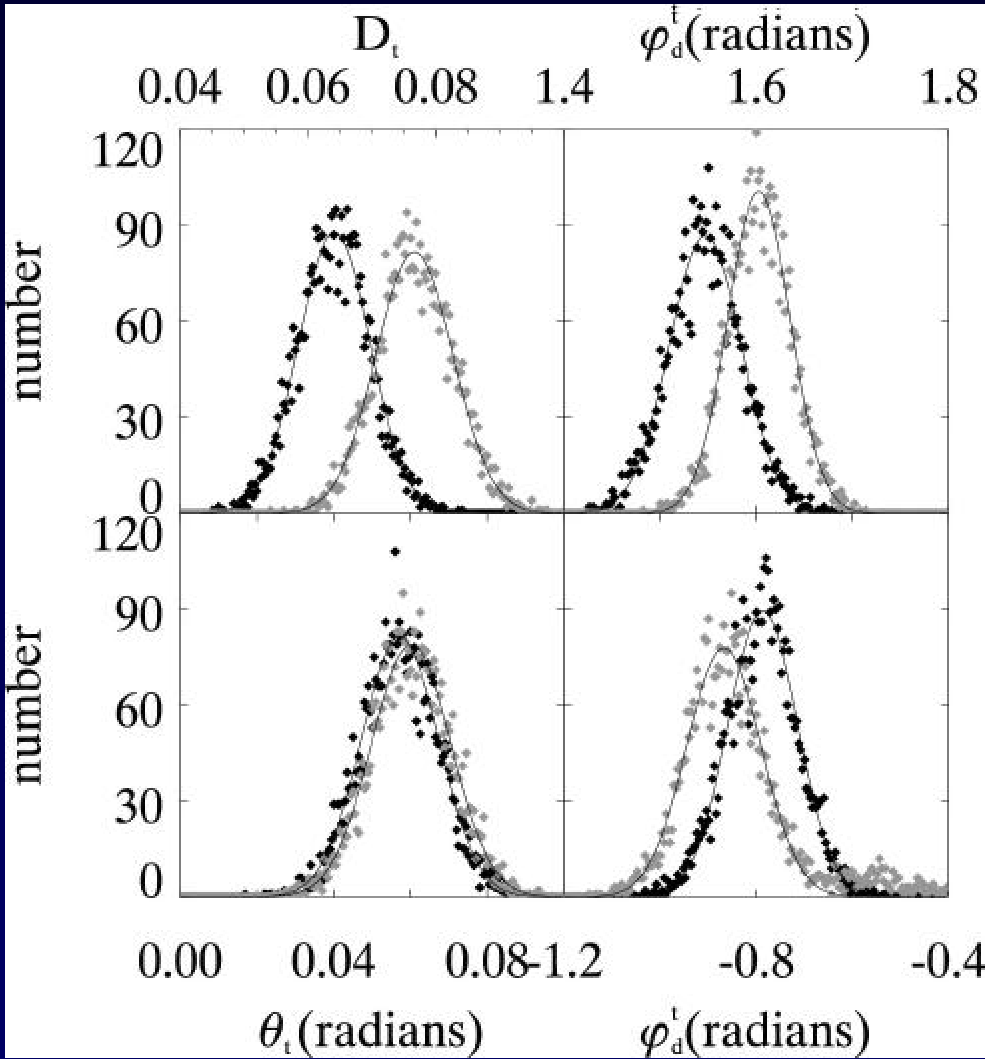
MEASUREMENT • ANALYSIS • INFORMATICS • DESIGN • FABRICATION •

NCMC

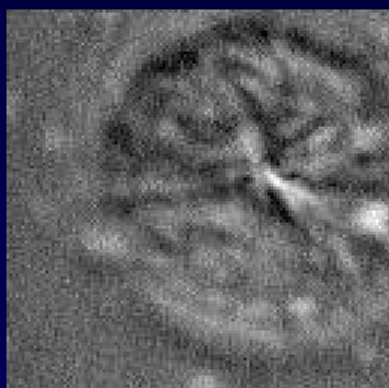
Nulling the polarimeter

NSOM tips are dichroic!
To some extent birefringence can be nulled using a “fiber polarization controller”



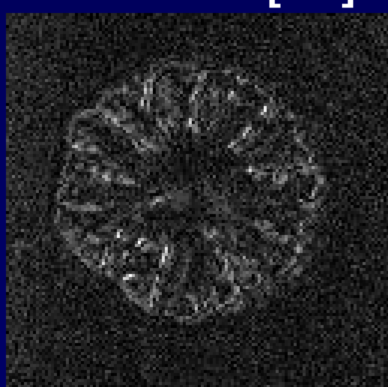


Dichroism [7%]

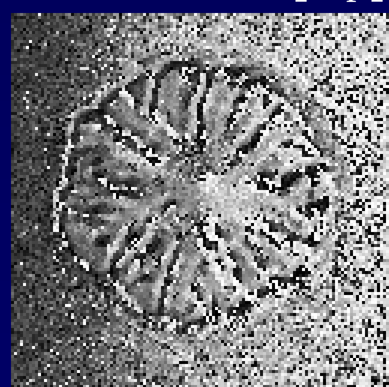


dichroic axis [0-p]

Dichroism [2%]



dichroic axis [0-p]



Polarimetry Formalism

$$\begin{pmatrix} E_x' \\ E_y' \end{pmatrix} = J \begin{pmatrix} E_x \\ E_y \end{pmatrix}$$

8 independent parameters needed to completely describe the fields and construct the Jones Matrix. Physical properties include:

Linear retardance (2): θ, ϕ_b

Linear dichroism (2): D=(x-y)/(x+y), ϕ_d

Circular retardance
Circular dichroism
Overall attenuation
Overall retardance

D(x,y),Linear diattenuator (dichroic), transmission coefficients x and y

$$\begin{pmatrix} \sqrt{x} & 0 \\ 0 & \sqrt{y} \end{pmatrix}$$

P, Linear polarizer, pass direction x

$$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$$

B(θ), Linear retarder, fast x axis, phase delay θ

$$\begin{pmatrix} e^{-iJ} & 0 \\ 0 & 1 \end{pmatrix}$$

PEM

$$\begin{pmatrix} e^{-idSin(wt)} & 0 \\ 0 & 1 \end{pmatrix}$$

QWR

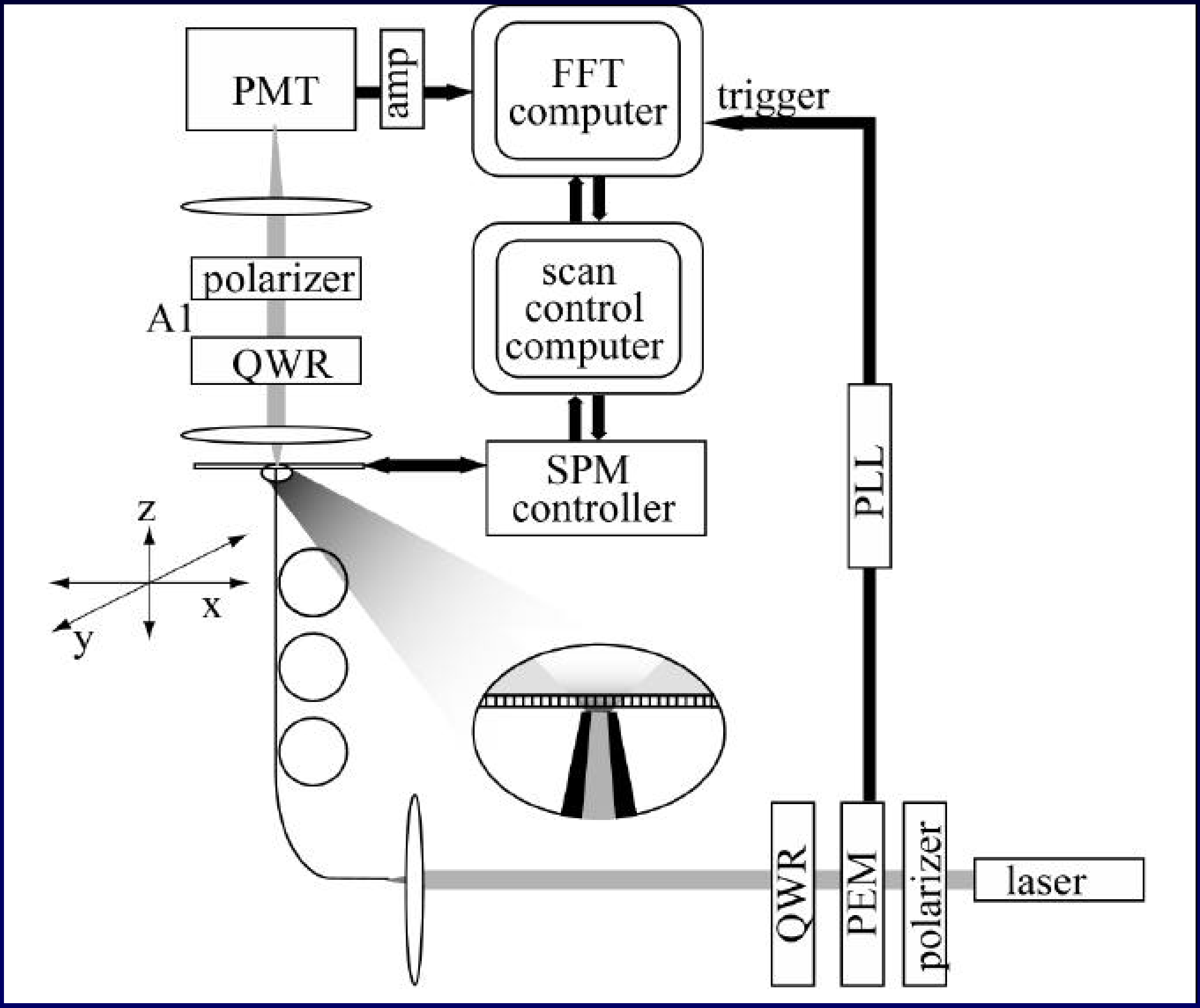
$$\begin{pmatrix} -i & 0 \\ 0 & 1 \end{pmatrix}$$

R(ϕ),Rotation through an angle ϕ from the x axis

$$\begin{pmatrix} Cos(f) & -Sin(f) \\ Sin(f) & Cos(f) \end{pmatrix}$$

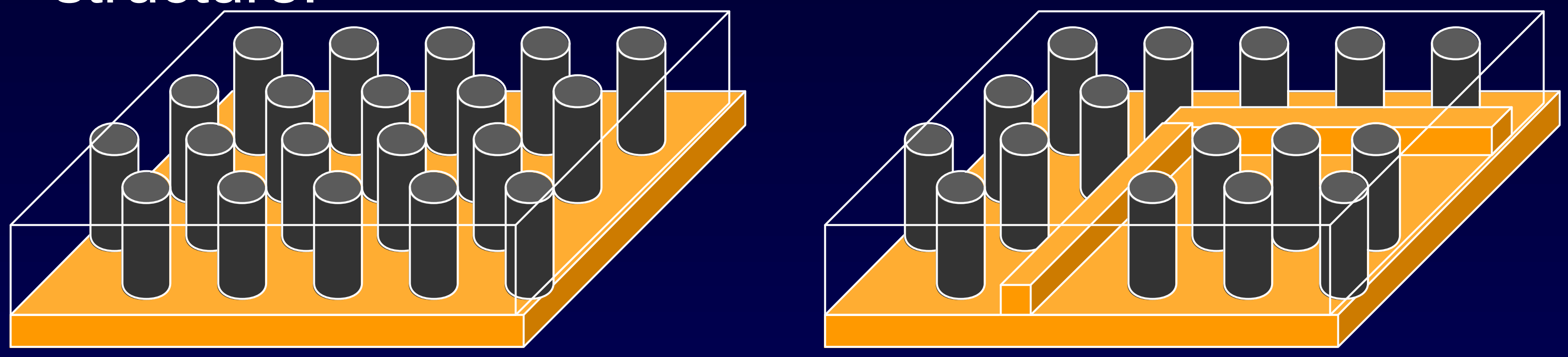
NSOM polarimeter

(For a similar system, see McDaniel et al *Applied Optics* **37**(1) p.84 1998)



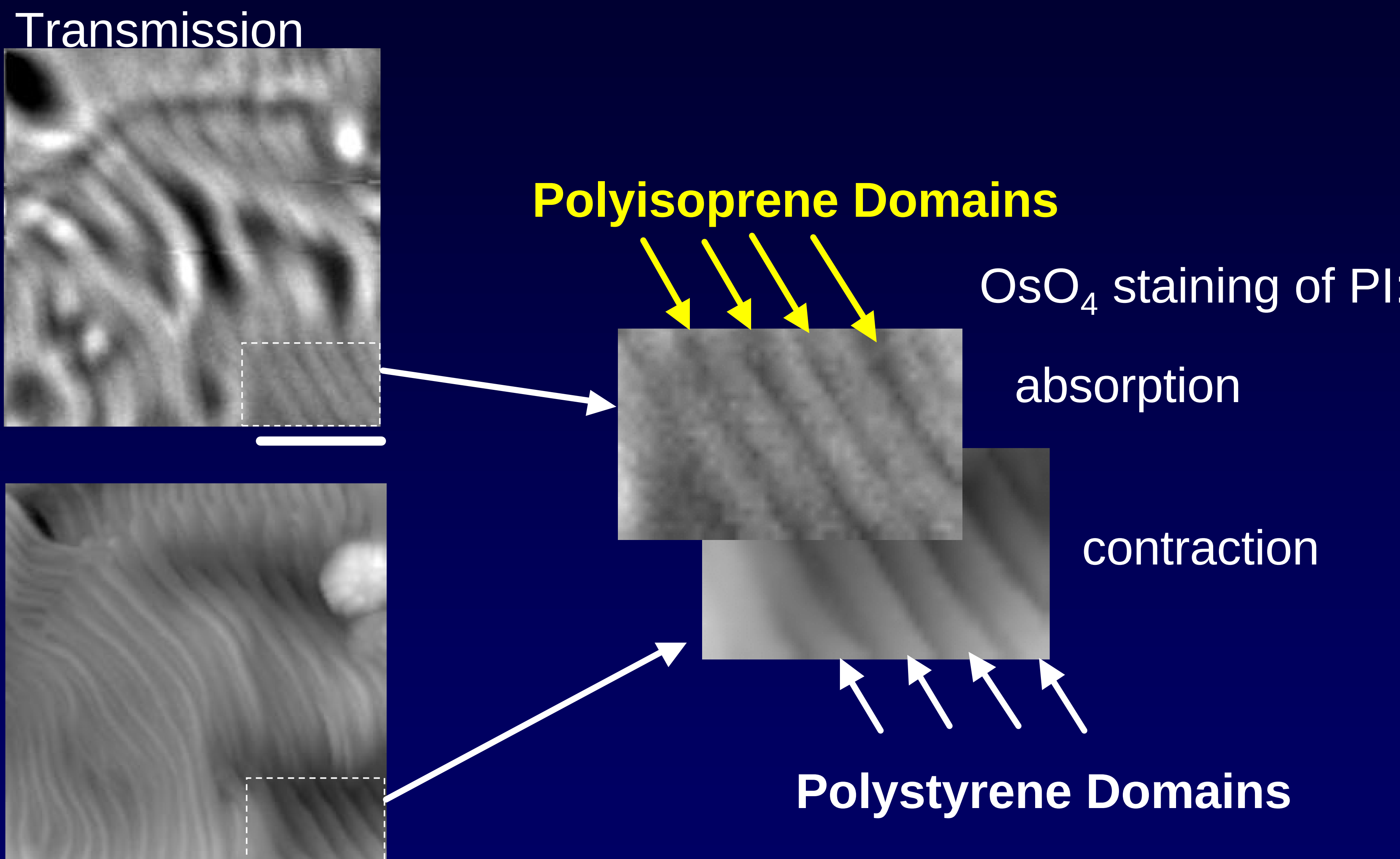
Photonic BC Thin Film Devices

- Thin BC films may exhibit in-plane 2D photonic band structure.



- Natural BC thin film morphology might be modified via patterned substrates, lithography or other means.
  - Controlled introduction of defects → e.g. wave guides/channels.
  - Modification/expansion of naturally occurring patterns → new photonic structures.
- Engineering of optical structure for device applications.

Domain identification



Scale bar: 1mm